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DEVELOPMENT OF FIRE RESISTANT  
WATER BASED HYDRAULIC FLUIDS

|                           |           |
|---------------------------|-----------|
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# ABSTRACT

Fire resistant, water based hydraulic fluid formulations have been evaluated for autoignition temperature, lubricity, static corrosion (determined from the liquid phase corrosion test) and for pump performance using a Vickers Vane Pump. In this report period, several large batches of alkanolamine borates and glycol borate condensates have been prepared for evaluation as well as a number of synthetic compounds containing boron and nitrogen.

## INTRODUCTION

Synthesized boron-nitrogen and glycol borate condensates have not only improved the fire resistance of many water based hydraulic fluids but have also acted as corrosion inhibitors on metals present in hydraulic pumps. These compounds are being utilized as additives to a water based hydraulic fluid base blend or as a substitute for a material in the blend.

Presently, additional data are being obtained to show the effect of selected additives on the autoignition temperatures of the base fluid blends. This study should define compatibility and effective concentration of the additives.

Vickers Vane Pump tests have been run in order to determine lubricity characteristics as well as the corrosive effects of some of the fluids on various metals under the dynamic test conditions in the pump reservoir. A preliminary check of the static liquid phase corrosion test of MIL-H-19457 specification has been run to obtain comparative data.

## SYNTHESIS OF IGNITION INHIBITORS

During the past several months, a complete series of alkanolamine borates have been prepared which have been screened as components of hydraulic fluids. The materials synthesized are polymeric in nature and water soluble for the most part. These compounds do not appreciably alter the viscosity of a finished water-glycol lubricant and only a few substantially increase fire resistance. The physical properties of the synthesized compounds are listed in Appendix Table I.

Our efforts are presently directed towards incorporating the alkanolamine esters into a water based hydraulic fluid which will meet all of the proposed target specifications. When 10 percent of the most promising candidate is added to an available commercial water glycol hydraulic fluid, the autogenous ignition temperature of the end product is increased by 75 to 100°F. Concentrations of inhibitor below 10 percent of the total fluid do not appear to be effective. The following table summarizes appropriate data.

### AUTOIGNITION INHIBITION OF A COMMERCIAL WATER GLYCOL HYDRAULIC FLUID

|   | <u>AIT, °F</u> |
|---|----------------|
| A - Commercial Water Glycol Hydraulic Fluid                                     | 765-775        |
| A + 5% DEAB   | 775-780        |
| A + 10% DEAB  | 860-870        |
| 10% Polyalkylene Glycol A<br>35% Polyalkylene Glycol B<br>10% DEAB<br>45% Water | 875-895        |
| 10% Polyalkylene Glycol A<br>35% Propylene Glycol<br>10% DEAB<br>45% Water      | 930-950        |

Alkanolamine borates, glycol borates and various other additives are being screened for compatibility and autoignition inhibition

properties in a promising hydraulic fluid base blend. Appendix Table II summarizes the evaluation. As brought out before, about 100°F increase in autoignition temperature is the greatest increase observed.

Vickers vane pump tests summarized below indicate that direct substitution of a glycol borate condensate for one of the polyalkylene glycols used in blend A produces a fluid (designated Blend J) which is deficient in lubricating properties. When only a partial substitution of the polyalkylene glycol in base A with the glycol borate condensate was effected, the resulting fluid had better lubricating qualities. This formulation is coded as base K. Further lubricity improvement in base K may be effected upon inclusion of appropriate antiwear additives. This phenomenon is demonstrated by the addition of a small amount of Benzotriazole and sodium benzoate (refer to results under Blend L). Blend L shows a vast improvement in lubricity characteristics over Blend J which is a similar formulation without wear additives.

|        | <u>Wear Rate, Ring</u> |
|--------|------------------------|
| Base A | 1.2 mg/hour            |
| Base J | 3000 mg/hour           |
| Base K | 17 mg/hour             |
| Base L | 16.6 mg/hour           |

Complete wear and formulation data are presented in Appendix Table III.

The effect of both lubricity and autoignition depressant additives on the pump performance of several water glycol hydraulic fluid bases is presented below. The addition of up to 8 percent of the synthesized P-Glyco Bor additive improves the lubricity characteristics of the resultant formulation.

|  | <u>Wear Rate, Ring</u> |
|--|------------------------|
| Blend B (including 1% sodium benzoate) | 4.0 mg/hour            |
|  | 0.2 mg/hour            |
| + 1% P-Glyco-Bor                       | 0.2 mg/hour            |
| + 4% P-Glyco-Bor                       | 0.1 mg/hour            |
| + 8% P-Glyco-Bor                       | 0.2 mg/hour            |

More detailed data are presented in Appendix Table IV

A preliminary check of the corrosivity of several fluid blends was conducted by examining the pump parts after test runs at 120° and 140°F. Blends J, K and L, all containing the synthesized P-Glyco-Bor additive, caused no visible corrosion to the pump parts. Blend C, which contains a commercial fire resistant, water soluble, phosphate additive, caused heavy corrosion to the steel pump parts. Blends A and B, both containing various percentages of several polyalkylene glycols in a water formula, cause moderate to heavy corrosion to the steel pump parts.

WATER GLYCOL BASE STOCKS RATED FOR CORROSIVITY  
DURING VICKERS VANE PUMP RUNS

| <u>Blend</u> | <u>Rating*</u> |
|--------------|----------------|
| A            | 4              |
| B            | 6              |
| C            | 10             |
| J            | 1              |
| K            | 1              |
| L            | 1              |

\* Ratings - 1 = Very good condition - No visible corrosion of pump parts

10 = Very poor condition - Rust and corrosion of pump parts is evident

A series of pump tests were conducted in order to show the effect of the formulated, water based hydraulic fluids on some of the metals. It is noted here that the addition of the P-Glyco Bor additive to Base Blend B containing sodium benzoate, lessens the attack of zinc plate. Data confirming this statement is presented in Appendix Table V.

A preliminary check of the static liquid phase corrosion test of MIL-H-19457 specification was run to obtain comparison data to the dynamic corrosion tests. It is again noted that the Zinc panel is clean and bright which is definitely due to the addition of the P-Glyco Bor additive added to the Base Blend B. These observations can be detailed in Appendix Table VI.

The following data represent initial studies of foam tendencies of three experimental fluids. Tested at 75°F and 140°F in order to determine what degree of foam can be expected from higher viscosity fluids specified in the proposed target requirements. The most promising hydraulic fluid formulation having the lowest foam tendency

will be considered the most acceptable. These data indicate that the P-Glyco Bor additive in conjunction with the high molecular weight glycol presents no foaming problem.

FOAM TENDENCY OF FLUIDS @ 75°F AND 140°F

|   |       | <u>Tendency<br/>ml of foam<br/>after 5 min<br/>aeration</u> | <u>Stability<br/>ml of foam after<br/>10 min of collapse<br/>time</u> |
|---|-------|---|---|
| Base A + 1% sodium benzoate                       | 75°F  | 550   | 190   |
|   | 140°F | 580   | None  |
| Base A + 1% sodium benzoate<br>0.1% benzotriazole | 75°F  | 550   | 190   |
|   | 140°F | 540   | None  |
| Base L  | 75°F  | 230   | 10  |
|   | 140°F | 510   | 20  |

## STATUS AND FUTURE PROGRAM

Ignition inhibitors, both the commercial and the experimental materials, have been screened for this project. Two types of compounds, glycol borates and alkanolamine borates, show the most promise for this application. These materials are now being prepared in sufficient quantities for the formulation and evaluation tests listed in the target specification.

The AIT apparatus, described in ASTM D 1255 T, has been constructed and will be used to confirm data we have determined by the procedure listed in ASTM D 286.



APPENDIX TABLE I

| Name                     | Appearance  | Neut No.   | PH-20% in H <sub>2</sub> O | Visc @ 100°F cs | Visc @ 100°F 20% in H <sub>2</sub> O cs | R I ND/20°C | Flash Pt (COC) | Fire Pt (COC)       | AIT°F   |
|--------------------------|---|------------|----------------------------|-----------------|---|-------------|----------------|---------------------|---------|
| 50 HB 660-Het            | Dark, Brown Liquid                                  | 21.2 Acid  | 2.7                        | 271.0           | separation                              | 1.4673      | 450°F          | 500°F               | 750-775 |
| Tri-THFB                 | Sample separated into 2 layers on standing-24 hours | 3.36 Base  | 6.0                        |                 |   |             | 250°F          | 290°F               | <700    |
| E-Glyco Bor              | Water wt. liquid                                    | 78.5 Base  | 8.4                        | 79.4            | 1.17                                    | 1.4422      | 240°F          | 260°F               | 950-970 |
| P-Glyco Bor Batch 1      | Clear, amber liquid                                 | 81.3 Base  | 8.4                        | 300.0           | 1.27                                    | 1.4400      |                | 220°F               |         |
| P-Glyco Bor Batch 2      | Clear, amber liquid                                 | 71.6 Base  | 8.4                        | 78.2            | 1.27                                    | 1.4331      |                | 280°F               | >1000   |
| P-Glyco Bor Batch 3      | Clear, amber liquid                                 | 70.0 Base  | 8.1                        | 131.75          | 1.262                                   | 1.4351      |                | 280°F               |         |
| P-Glyco Bor Batch 4      | Cloudy fluid  | 60.6 Base  | 8.3                        |                 |   | 1.4310      |                |                     |         |
| D-Glyco Bor Amine in P-G | Yellow to Brown semi solid                          | 267.5 Base | 10.0                       |                 |   |             |                | 130°F Recheck 120°F |         |

Appendix Table I continued

| Name           | Appearance                     | Neut No.  | PH-20% in H <sub>2</sub> O | Visc @ 100°F CS | Visc @ 100°F 20% in H <sub>2</sub> O CS | R I ND/20°C | Flash Pt (COC) | Fire Pt (COC) | Alt°F   |
|----------------|--------------------------------|-----------|----------------------------|-----------------|---|-------------|----------------|---------------|---------|
| 75 H 450 Bor   | Brown liquid                   | 2.52 Base | 7.2                        | 141.4           | 2.368                                   | 1.4645      | 500°F          | 610°F         | 760-775 |
| PHPC           | Clear, amber liquid            | 8.9 Base  | 9.75                       | 90.96           | 1.356                                   | 1.4481      |                |               | 960-975 |
| PPCB-A         | Cloudy solid                   |           | 5.15                       |                 | separated in H <sub>2</sub> O           |             |                |               | 790-810 |
| MEAB-A Batch 1 | Cloudy, viscous polymeric type | 740 Base  | 10.1                       |                 | 1.497                                   |             |                |               | 835-855 |
| MEAB-A Batch 2 | Viscous-polymeric type         | 700 Base  | 10.5                       |                 | 1.574                                   | 1.4885      |                |               | 970     |
| MEAB Batch 1   | Viscous-polymeric type         | 605 Base  | 9.6                        |                 |   | 1.4994      |                |               | 815-890 |
| MEAB Batch 2   | Viscous-polymeric type         | 435 Base  | 9.9                        |                 |   |             |                |               | 970     |
| DEAB-A Batch 2 | Viscous-polymeric type         | 523 Base  | 9.6                        |                 | 1.824                                   | 1.4990      |                |               |         |
| DEAB-A Batch 3 | Viscous-polymeric type         | 504 Base  | 9.7                        |                 | 1.515                                   | 1.4955      |                |               | 775     |

Appendix Table I continued

| Name         | Appearance             | Neut. No. | PH-20% in H <sub>2</sub> O | Visc @ 100°F in CS | Visc @ 20% in H <sub>2</sub> O in CS | R I ND/20°C | Flash Pt (COC) | Fire Pt (COC) | AIT°F |
|--------------|------------------------|-----------|----------------------------|--------------------|--------------------------------------|-------------|----------------|---------------|-------|
| DEAB Batch 2 | Viscous-polymeric type |           |                            |                    |                                      |             |                |               |       |
| DEAB Batch 3 | Viscous-polymeric type | 202 Base  | 6.2                        | 1.239              | 1.4734                               |             |                |               | 925°+ |
| DEAB Batch 4 | Viscous-polymeric type | 252 Base  | 8.2                        | 1.19               | 1.4760                               |             |                |               | 970   |
| MIPAB-A      | Viscous-polymeric type | 645 Base  | 10.5                       |                    |                                      |             |                |               |       |
| NIPAB        | Viscous-polymeric type | 365 Base  | 9.5                        | 1.09               | 1.4686                               |             |                |               |       |
| DIPAB-A      | Viscous-polymeric type |           |                            |                    |                                      |             |                |               |       |
| DIPAB        | Viscous-polymeric type | 224.4     | 7.9                        | 1.098              | 1.4616                               |             |                |               | 825°  |
| TIPAB-A      | Viscous-polymeric type | 126.2     | 8.8                        | 1.359              | 1.4678                               |             |                |               |       |
| TIPAB        | Viscous-polymeric type | 112.2     | 8.8                        | 1.270              | 1.4592                               |             |                |               |       |

Solidified during reaction - discontinued

APPENDIX TABLE II

AUTOIGNITION INHIBITION OF A GLYCOL BASED  
HYDRAULIC FLUID THROUGH ADDITIVE TREATMENT

Selected Base Fluid

16% Polyalkylene Glycol (a)  
39% Polyalkylene Glycol (b)  
45% Water

| <u>Additive Treatment</u> |                                | <u>AIT°F</u> |
|---------------------------|--------------------------------|--------------|
| 1.                        | None                           | 830          |
| 2.                        | 4% Potassium Diethyl Phosphate | 805          |
| 3.                        | 4% GB DEA Complex              | 840          |
| 4.                        | 4% DEAB - Batch 1              | 870-935      |
| 5.                        | 4% E. Glyco-Bor - Batch 1      | 845          |
| 6.                        | 4% DEAB-A - Batch 1            | 815          |
| 7.                        | 10% DEAB-A - Batch 3           | <825         |
| 8.                        | 10% MEAB - Batch 2             | 825          |
| 9.                        | 4% Urea                        | 830          |
| 10.                       | 8% Urea                        | <840         |
| 11.                       | 5% MIPAB                       | <805         |
| 12.                       | 10% DIPAB-A                    | 810          |
| 13.                       | 20% DIPAB-A                    | 895          |
| 14.                       | 30% DIPAB-A                    | 835          |
| 15.                       | 40% DIPAB-A                    | <800         |
| 16.                       | 10% DIPAB                      | <810         |
| 17.                       | 20% DIPAB                      | 800          |
| 18.                       | 10% TIPAB-A                    | 785          |
| 19.                       | 20% TIPAB-A                    | 760          |
| 20.                       | 30% TIPAB-A                    | 835          |
| 21.                       | 40% TIPAB-A                    | 845          |
| 22.                       | 10% TIPAB                      | 760          |
| 23.                       | 20% TIPAB                      | 925          |
| 24.                       | 40% TIPAB                      | 875          |

APPENDIX TABLE III  
SCREENING PUMP TESTS OF FLUID BLENDS

Vickers V-104-A-10 Pump

Pressure 900 psi  
 Vol. output 5 GPM  
 Operating Temp 115-125; 130-145°F

|                         |                | <u>Hours</u> | <u>Wear, mg</u><br><u>Ring</u> | <u>Vanes</u> |
|-------------------------|----------------|--------------|--------------------------------|--------------|
|                         | <u>Blend J</u> |              |                                |              |
| Polyalkylene Glycol (a) | 21%            |              |                                |              |
| P-Glyco Bor Batch 2     | 34%            |              |                                |              |
| Water                   | 45%            | 3            | 9050                           | 942          |
|                         | <u>Blend K</u> |              |                                |              |
| Polyalkylene Glycol (a) | 16.5%          |              |                                |              |
| Polyalkylene Glycol (b) | 29.5%          |              |                                |              |
| P-Glyco Bor Batch 3     | 8.0%           | 18           | 183                            | 24           |
| Water                   | 45 %           | 22           | 89                             | 33           |
| Sodium Benzoate         | 1.0%           | 65           | 19                             | 12           |
|                         | <u>Blend L</u> |              |                                |              |
| Polyalkylene Glycol (c) | 16.0 %         |              |                                |              |
| P-Glyco Bor Batch 4     | 35.95%         |              |                                |              |
| Water                   | 45.0 %         |              |                                |              |
| Sodium Benzoate         | 1.0 %          | 16           | 273                            | 1            |
| Benzotriazole           | 0.05%          | 23           | 383                            | 0            |

APPENDIX TABLE IV

EFFECT OF ADDITIVE MATERIALS ON THE  
PUMP PERFORMANCE OF THE BASE FLUIDS

| <u>Fluid</u>   | <u>Hours</u> | <u>Wear, mg</u> |              |
|--|--------------|-----------------|--------------|
|  |              | <u>Ring</u>     | <u>Vanes</u> |
| Blend B + 1% Sodium Benzoate<br>Test Stand No. 1         | 18           | 47              | 41           |
|  | 22           | 39              | 25           |
|  | 18           | 9               | 8            |
|  | 65           | 2               | 4            |
| Blend J + 1% EFH Additive                                | 18           | 213             | 4            |
|  | 9            | 150             | 3            |
| Rerun of above fluid                                     | 19           | 377             | 1            |
|  | 21           | 397             | 2            |
| Blend J + 2% EFH Additive                                | 24           | 432             | NWL          |
|  | 22           | 423             | 4            |
| Blend B + 1% Sodium Benzoate<br>+ 1% P-Glyco bor Batch 3 | 19           | 5               | 1            |
| Blend B + 1% Sodium Benzoate<br>+ 4% P-Glyco bor Batch 3 | 65           | 8               | 7            |
| Blend B + 1% Sodium Benzoate<br>+ 8% P-Glyco bor Batch 3 | 18           | 3               | 2            |

APPENDIX TABLE V

STUDY OF METALS CORROSION IN LIQUID PHASE  
IMMERSION TESTS DURING PUMP OPERATION

Immersion @ 140°F in reservoir of hydraulic pump stand  
Test panels - 1x1x1/16; Zinc plate 1x2x1/16

Fluid - Blend B + 1% Sodium Benzoate  
Duration - 20 hrs

|            | <u>Weight Change, mg</u> |
|------------|--------------------------|
| Aluminum   | -0.2                     |
| Copper     | +0.4                     |
| Bronze     | None                     |
| Steel      | +0.2                     |
| Zinc plate | -2.8 evidence of attack  |
| Zinc plate | -0.3 on Zinc plate       |

Fluid - Blend B + 1% Sodium Benzoate  
+ 1% P-Glyco bor Batch 3  
Duration - 20 hrs

|            |      |
|------------|------|
| Aluminum   | +0.1 |
| Copper     | +0.4 |
| Bronze     | +0.7 |
| Steel      | +0.2 |
| Zinc plate | -1.2 |
| Zinc plate | None |

Fluid - Blend B + 1% Sodium Benzoate  
+ 4% P-Glyco bor Batch 3  
Duration - 65 hrs

|          |      |
|----------|------|
| Aluminum | -0.8 |
| Copper   | +0.1 |
| Bronze   | -0.3 |
| Steel    | +2.7 |
| Zinc     | -0.6 |

APPENDIX TABLE VI

STATIC CORROSION LIQUID PHASE CORROSION TEST

MIL-H-19457

Duration - 1 week  
Test Temp - 130°F

Fluid - Blend B + 1% Sodium Benzoate

| <u>Metal</u> | <u>Weight Change, mg/mg/cm<sup>2</sup></u> | <u>Appearance</u>      |
|--------------|--|------------------------|
| Aluminum     | -0.3/0.009                                 | Clean and bright       |
| Bronze       | +0.4/0.012                                 | Hazy film              |
| Steel        | -0.5/0.015                                 | Clean and bright       |
| Copper       | +1.9/0.056                                 | Dulling film - bronzed |
| Zinc         | -2.3/0.067                                 | Dulled surface         |

Fluid - Blend B + 1% Sodium Benzoate  
+ 4% P-Glyco bor Batch 3

|          |            |                               |
|----------|------------|-------------------------------|
| Aluminum | -1.0/0.030 | Scattered gray black staining |
| Bronze   | -1.0/0.030 | Clean and bright              |
| Steel    | -0.8/0.021 | Slightly dulled surface       |
| Copper   | +1.1/0.032 | Dulling film - bronzed copper |
| Zinc     | -1.6/0.047 | Clean and bright              |

Fluid - Blend B + 1% Sodium Benzoate  
+ 8% P-Glyco bor Batch 3

|          |            |   |
|----------|------------|---|
| Aluminum | -0.2/0.006 | Gray-black staining slightly more than in fluid above |
| Bronze   | -0.4/0.012 | Clean and bright                                      |
| Steel    | -0.4/0.012 | Clean and bright                                      |
| Copper   | +1.1/0.032 | Dulling film; bronzed                                 |
| Zinc     | -1.7/0.050 | Clean and bright                                      |